

# **Does Conventional Nucleation Occur During Phase Separation in Polymer Blends?**

Nitash P. Balsara<sup>1,2</sup>, Timothy J. Rappl,<sup>1</sup> Amy A. Lefebvre,<sup>1</sup>

<sup>1</sup>Department of Chemical Engineering, University of California, Berkeley, California 94720

<sup>2</sup>Material Sciences Division, and Environmental Energy Technologies Division, Lawrence Berkeley National Laboratory, University of California, Berkeley, California 94720

## **Summary of Presentation**

We have completed a comprehensive study of the equilibrium and non-equilibrium thermodynamic properties of off-critical, high molecular weight polymer blends using static and time-resolved small angle neutron scattering. Our objective was to observe the formation of critical nuclei during the initial stages of liquid-liquid phase separation. Previous studies on the initial stages of liquid-liquid phase separation in polymer blends have focused on critical blends undergoing spinodal decomposition. We chose polymethylbutylene/polyethylene blends because the phase behavior of this system follows the well-known Flory-Huggins theory, and can thus be readily modeled. We found good agreement between the binodal and spinodal curves obtained from theory and experiment. We then studied the kinetics of phase separation, focusing on quenches into the metastable region of the phase diagram that is bounded by the binodal and spinodal curves.

We established that the scattering from structures formed during the initial stages of phase separation is consistent with the Ornstein-Zernicke equation. The Ornstein-Zernicke parameters obtained from all of the blends obey a universal scaling law, indicating that structures responsible for nucleation are diffuse, self-similar and their characteristics are independent of quench depth. We found

that the scattering profiles obtained during phase separation were independent of time for scattering vectors,  $q$ , greater than a critical scattering vector,  $q_c$ . We concluded that the growing structures during the initial stages of nucleation must have length scales greater than  $1/q_c$ , the lower limit of the length scale of the structures responsible for the initial phase separation process  $R_c=1/q_c$ . We found that  $R_c$  decreased monotonically with increasing quench depth. A major prediction of conventional nucleation theories is the divergence of the critical nucleus size at the spinodal. We found no evidence of such a divergence. We thus conclude that the spinodal, defined as the quench depth at which the static structure factor of a mixture diverges, appears to have no dynamic significance.

Our work indicates that the nucleation pathways in polymer blends are not consistent with any of the available theoretical predictions. Many of our observations are, however, consistent with simulations of nucleation in an Ising magnet where fluctuations are taken into account explicitly.

Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the ACS, the Department of Energy (Polymer Program of the Materials Sciences Division of Lawrence Berkeley National Laboratory), and the National Science Foundation (Grant No. CTS-305711) for support of this research. We acknowledge the support of the National Institute of Standards and Technology, U.S. Department of Commerce, in providing facilities used in this work. The SANS instrument is supported by Grant No. DMR-9986442 from the National Science Foundation to NIST.